MONITORING OF POLYBROMIATED DEPHENYL ETHERS IN SEDIMENTS OF HAN RIVER IN KOREA

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Introduction

Recently Polybrominated diphenyl ethers (PBDEs) were introduced to be contained by a new POPs. PBDEs are used as flame retardant additives in polymers at range of 5~30% in various use, for example electronic and electrical appliances, computers, televisions, building materials and textiles. In Korea, There are three Commercial PBDEs products which are deca-brominated diphenyl ether (Deca-BDE), octa-brominated diphenyl ether(Octa-BDE), penta-brominated diphenyl ether(Penta-BDE) and domestic import at 2003 of these were 9015tons, 226tons and 26.3tons individually[1].

The similarity in Molecular structure of PBDEs with PCBs and PCDD/Fs rise to concern that they may lead to similar environmental problems. Actually, there are hot environmental concern because of recent study for toxicity and increase of concentration in human body and organism.

This study aims to examine the levels of PBDEs and understand the characteristics of PBDEs contamination in Han River, Korea.

Materials and Methods

Sample collection

The area of this study is Han River which is the secondary river (26,219Km^2, length: 497.5km) in South Korea. Surface sediment was collected from 6 sites of Han River by means of a hand-held grab sampler (iron steel) and placed in glass jars. Immediately after collection, the samples were hexane-washed aluminum foil was placed over the mouth of the jar and transported to the laboratory by dry ice. Surface sediment samples were dried at room temperature prior to analysis. All samples were collected on October 2004.

Extraction and cleanup

Surface sediment samples were weighted at extraction thimble. Same amount of anhydrous sodium sulfate was added and mixed with the sediment. The samples were extracted using a Soxhlet extractor.

Two types of solvent which were in order Hexane/acetone (1:1, v/v), Toluene were used in extraction. The extracts were spiked with a mixture of $^{13}C_{12}$-PBDEs (Mo-Hp;1ng, Octa-Nona;2.5ng, Deca;5ng) as the

Cleanup spike. The extracts were cleaned up using a Multi-layer silica-gel eluted with 15% dichloromethane in hexane. And the next step is Dispose of DMSO. Final extracts were concentrated to and spiked with $^{13}C_{12}$-HxBDE(#139)1ng as syringe spike. Instrumental analysis was conducted with HRGC-HRMS using the SIM(Selcted Ion Monitoring) method.

Results and Discussion

Concentraion of PBDEs

The total PBDEs concentrations in sediments ranged from 10.18 to 46.58 ng/g d.w. as shown in Table 1. The average value of concentration is 28.46 ng/g d.w(n=6). All sites had detected indicating that these pollutants have reached the river or there is possibility of industrial activities. The highest concentrations of PBDEs were found in site SS which are in close proximity to industrial and residential area.

Table 1. Concentration of PBDEs in surface sediment of Han river in Korea (unit : pg/g)

	SS	YH	SG	WH	HG	BP
BDE-3	<100	<100	<100	<100	<100	<100
BDE-7	39	16	33	46	<10	20
BDE-15	56	78	82	86	54	55
BDE-17	230	200	230	240	110	120
BDE-28	150	<10	120	240	160	98
BDE-49	1000	1100	910	1400	760	700
BDE-71	<10	<10	<10	<10	<10	<10
BDE-47	4400	5200	3000	8000	3800	3600
BDE-66	140	<10	130	270	220	200
BDE-77	<10	<10	<10	<10	<10	<10
BDE-100	1000	1900	640	2300	800	1300
BDE-119	57	<10	<10	65	62	<10
BDE-99	5600	9700	3000	9400	5200	6400
BDE-85	160	<10	68	310	180	200
BDE-126	<10	<10	<10	<10	<10	<10
BDE-154	490	880	220	890	460	580
BDE-153	750	1200	220	750	800	810
BDE-138	70	130	<10	<10	62	77
BDE-183	280	170	<30	51	230	170
BDE-197	<100	<100	<100	<100	130	160
BDE-196	240	150	<100	<100	160	190
BDE-207	1400	630	<100	100	830	210
BDE-206	2700	790	<100	140	1400	220
BDE-209	26000	8900	1200	1000	22000	1200
MoBDEs	<100	<100	<100	<100	<100	<100
DiBDEs	140	160	180	180	77	100
TrBDEs	460	300	460	570	330	270
TeBDEs	5600	6300	4100	9900	4900	4600
PeBDEs	6800	12000	3800	12000	6300	7900
HxBDEs	1400	2300	440	1700	1400	1500
HpBDEs	310	170	<30	51	230	340
OBDEs	870	430	<100	180	540	820
NBDEs	5000	1800	<300	310	2800	580
DeBDE	26000	8900	1200	1000	22000	1200
Total PBDEs	46580	32360	10180	25891	38577	17310

The levels of PBDEs found in the Han river sediment are similar to those found in Virginia superficial sediments at levels ranging from 0.5 to 52.3 ng/g and lower than those found in Niagara river sediments at levels ranging from 0.72 to 148 ng/g [2]. Also, our results are similar to those of river basins found in Portugal ranging 0.4~18 ng/g for sum of BDE-47, BDE-99 and BDE-100 which congeners detected in environmental samples in general[3].

Congener profile of PBDEs

Congener profile of PBDEs in sediment of this study was shown in Fig. 1. The congener patterns of all sediment samples were similar with each other. In particular, the major congeners which dominate total PBDEs as 65~80% were BDE-47, BDE-99 and BDE-209. Minor congeners which contribute 13~22% to total PBDEs were BDE-49, BDE-100, BDE-153, BDE-154, BDE-206 and BDE-207. The other congeners were contributed 6~13%. So, congener profile in this area is similar to Penta-BDE mixture as shown in Table 2. Also, existences of BDE-209, BDE-207, and BDE-206 imply a traceability of Deca-BDE mixture usage.

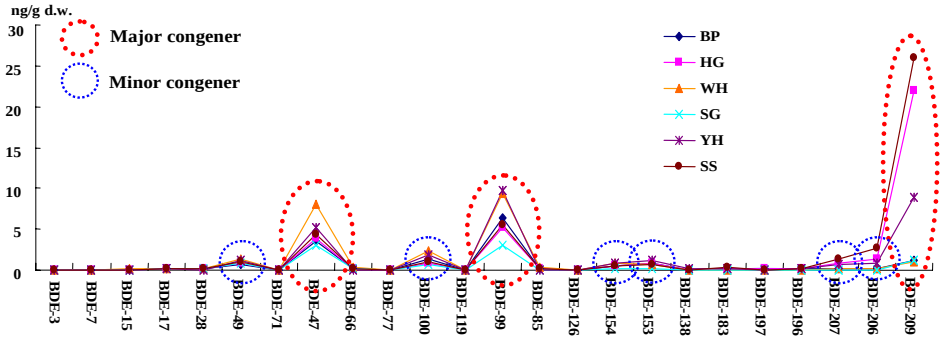

Fig. 1. Congener profile of PBDEs in sediment of this study

The congener pattern of sediment of Han River is almost consistent with Penta-BDE mixture but not Octa-BDE mixture as shown in Figure 2.

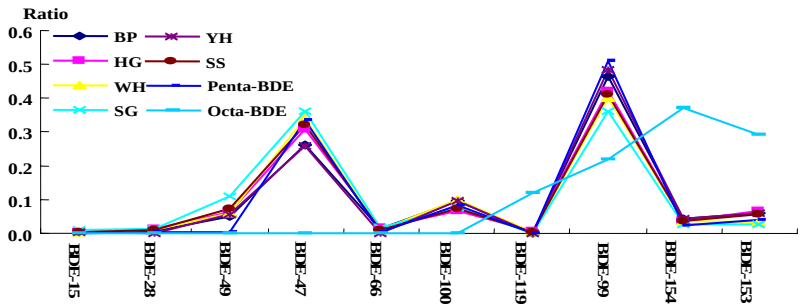

Fig. 2 Comparison of congeners with this study and PBDEs products

As a result, sediments of Han River were contaminated to some degree by PBDEs because results of this study were alike concentrations which were contaminated by industrial and economic activities other countries. Also, congener patterns were found in sediment of this study result from present inputs of the Penta- and Deca-BDE mixture. This represents that those mixtures are source of contamination. Especially, PBDE congener patterns observed in sediment of SS, which was detected as the highest concentration of this study, near urban and industrial regions arise from Penta- and Deca-BDE mixture because of some more present use as compared with other site of this study [4].

Table 2. Congener information of PBDEs products[5,6]

Congeners	Bromkal 70-5DE (Penta-BDE mixture)	Bromkal 79-8DE (Octa-BDE mixture)	Dow FR300 BA (Deca-BDE mixture)
Major	47, 99	183, 197, 207, 209	209
Minor	100, 153, 154, 85	203, 196, 208, 206	206, 207
Trace	138, 66, 28, 17, 183	204	208
Other	49, 74, 101, 97/118, 155, 139, 140	181, 191, 173/190, 205	

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